DOI: 10.1002/ejic.201000186

Coupling of Silsesquioxane Cages in the Coordination Sphere of Erbium

Volker Lorenz,[a] Steffen Blaurock,[a] Cristian G. Hrib,[a] and Frank T. Edelmann*[a]

Dedicated to Professor Karl-Heinz Thiele on the occasion of his 80th birthday

Keywords: Lanthanides / Silsesquioxanes / Metallasilsesquioxanes / Erbium / Cluster compounds

A novel transformation of silsesquioxane cages in the coordination sphere of a lanthanide ion is reported. Reaction of in situ prepared $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$ with anhydrous $ErCl_3$ in thf solution afforded the large heterometallic (Er/Li) metallasilsesquioxane cluster $(c\text{-}C_6H_{11})_{21}Si_{21}O_{36}(SiMe_3)Er_2(thf)_2Li_4Cl_2$ (**2**) in good yield (65 %). The molecular structure of **2** comprises several unusual features, including the coupling of two silsesquioxane cages through an $–O_3Si(c\text{-}C_6H_{11})–$ unit as well as trimethylsilylation of an Si–OH functionality. Due to the presence of 21 cyclohexyl substituents in the periphery of the molecule, the large cluster compound is soluble even in pentane.

Introduction

Polyhedral oligosilsesquioxanes of the general formula $(RSiO_{1.5})_n$ form an unusual and interesting class of organosilicon compounds, which currently have a strong impact on both catalysis research[1,2] and materials science.[3] In accordance with several unique properties, the polyhedral silsesquioxanes have been termed the “smallest particles of silica possible”[4] or “small soluble chunks of silica”.[2] With respect to catalysis research the chemistry of metallasilsesquioxanes also receives considerable current interest.[1,2,5,6] Incompletely condensed silsesquioxanes such as $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (**1**) share far-reaching structural similarities with β-tridymite and β-cristobalite and are thus quite realistic models for the silanol sites on silica surfaces.[1,2,6–11] Metal complexes derived from **1** are therefore commonly regarded as “realistic” models for industrially important metal catalysts immobilized on silica surfaces.[1,2,7]

The “Periodic Table of Metallasilsesquioxanes”[1b] already covers numerous metallic elements ranging from alkali metals[1,12,13] through early[1,14–18] and late transition metals[1,19–22] to the lanthanide elements.[1,23–27] Information on well-characterized lanthanide silsesquioxane derivatives is still quite limited. Very recently, a tetrameric neodymium silsesquioxane complex was prepared and structurally characterized by single-crystal X-ray diffraction.[28] We report here the formation and structural characterization of another very large lanthanide silsesquioxane cluster, which was obtained in an unexpected manner by treatment of anhydrous erbium(III) trichloride with in situ prepared $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$.

Results and Discussion

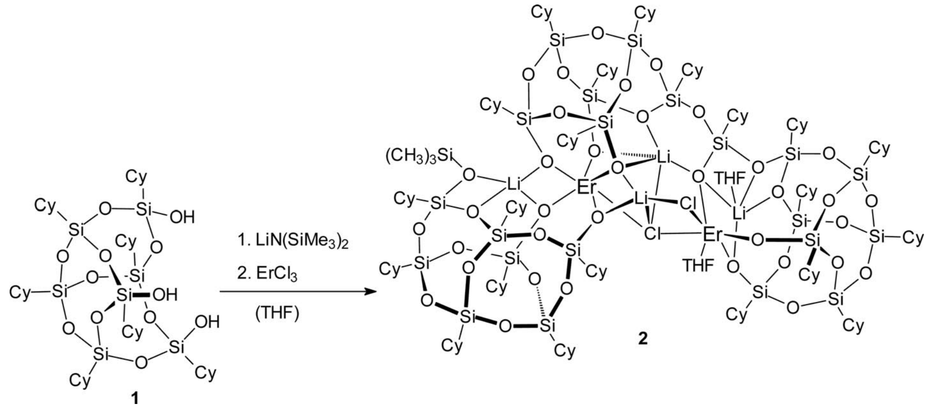
In a previous contribution[13] we have shown that the fully lithiated silsesquioxane derivative $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$ is an excellent precursor for the synthesis of novel heterodimetallic metallasilsesquioxanes. For example, the ytterbium bis(trimethylsilylamide) derivative $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Li_4]YbN(SiMe_3)_2$ was prepared in 51% isolated yield by treatment of in situ prepared $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$ with anhydrous $YbCl_3$.[13] Surprisingly, when carried out under very similar conditions, the analogous reaction of $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$ with anhydrous *erbium* trichloride took an entirely different course. $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$ was first generated by metalation of $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (**1**) with 3 equiv. of $LiN(SiMe_3)_2$, followed by reaction with anhydrous $ErCl_3$ in thf (Scheme 1).[29] Insoluble by-products were separated by extraction with *n*-pentane. Crystallization of the crude product from the same solvent afforded pale pink crystals in 65% isolated yield (determined after the crystal structure had been elucidated by X-ray diffraction). Meaningful ^1H and ^{13}C NMR spectroscopic data could not be obtained due to the paramagnetism of the Er^{3+} ion. The presence of eight resonances in the ^{29}Si NMR spectrum indicated a rather unsymmetrical molecular structure.

In the IR spectrum of **2**, a very strong and broad band at 1112 cm^{-1} is attributable to the ν(Si–O) vibrations, whereas a band at 1253 cm^{-1} provided some indication for the presence of an $–OSiMe_3$ functionality in the product.

---

[a] Chemisches Institut, Otto-von-Guericke-Universität Magdeburg,
Universitätsplatz 2, 39106 Magdeburg, Germany
Fax: +49-391-67-18327
E-mail: frank.edelmann@ovgu.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000186.



Scheme 1. Synthesis of $(c\text{-}C_6H_{11})_{21}Si_{21}O_{36}(SiMe_3)Er_2(thf)_2Li_4Cl_2$ (**2**).

Fortunately, pink single-crystals of **2** suitable for X-ray diffraction could be grown by slow cooling of a saturated solution in *n*-pentane to –20 °C. The X-ray analysis[30] confirmed the presence of a very unsymmetrical heterodimetallic molecule as suggested by the ^{29}Si NMR spectroscopic data. The molecular structure of **2** (Figure 1) comprises a large array of three silsesquioxane cages attached to two Er^{3+} and four Li^+ ions. Due to the presence of 21 cyclohexyl substituents in the periphery of the molecule, the large cluster compound is soluble even in pentane. Formally, the compound can be regarded as an "ate" complex formed by retention of 2 equiv. of LiCl in the product. Several unexpected structural features make this large cluster molecule quite unique. Most remarkable is the coupling of two silsesquioxane cages in the coordination sphere of the erbium atom. This results from opening of one Si–O–Si corner of the central silsesquioxane ligand and linking of two silsesquioxane cages through an $–O_3Si(c\text{-}C_6H_{11})–$ unit. This results in the formation of a novel hexaanionic $(c\text{-}C_6H_{11})_{14}Si_{14}O_{24}{}^{6–}$ bis(silsesquioxane) ligand attached to two Er^{3+} and four Li^+ ions. The third silsesquioxane cage is formally dianionic due to trimethylsilylation of one Si–OH functionality. The presence of an $–OSiMe_3$ group confirms the assumption gained from the IR data. The formation of this trimethylsilylated ligand can be explained by the presence of hexamethyldisilazane, $HN(SiMe_3)_2$, in the reaction mixture, which is formed during the initial metalation of **1** with $LiN(SiMe_3)_2$ (Scheme 1). Also quite remarkably, the coordina-

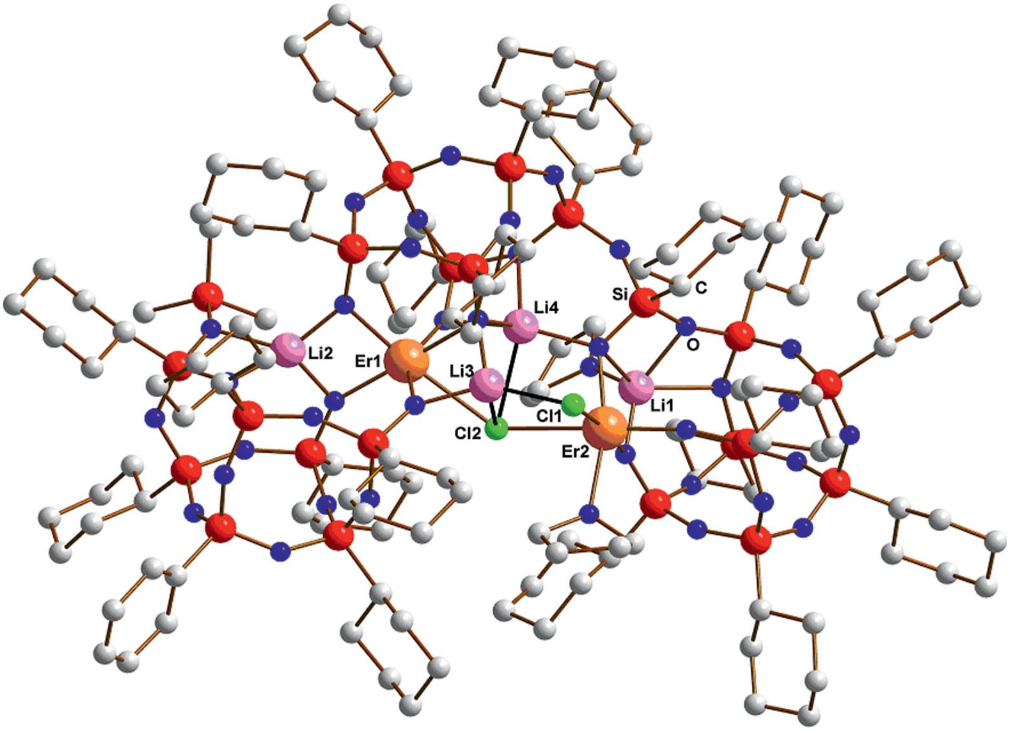


Figure 1. Molecular structure of $(c\text{-}C_6H_{11})_{21}Si_{21}O_{36}(SiMe_3)Er_2(thf)_2Li_4Cl_2$ (**2**). Selected bond lengths [Å]: Er1–O4 2.235(3), Er1–O13 2.188(2), Er1–O1 2.190(3), Er1–O15 2.323(3), Er1–O16 2.183(3), Er1–Cl2 2.856(1), Er2–Cl2 2.770(1), Er2–Cl1 2.679(1), Er2–O27 2.079(3), Er2–O24 2.230(2), Er2–O26 2.201(3). Er2–OL1 2.382(3), Li3–Cl1 2.272(7),Li3–Cl2 2.780(8), Li4–Cl2 2.670(7), Si–O 1.585(3)–1.650(3).

tion environments of all four lithium ions in **2** are different, with two of them being four-coordinate (LiO_4 and LiO_2Cl_2) and the other two five-coordinate (LiO_5 and LiO_4Cl).

The Er–O(Si) bond lengths in **2** are in the range of 2.183(3)–2.235(3) Å. These values are comparable to the Ln–O(Si) distances normally observed in organolanthanide siloxide complexes, for example, 2.170(2) Å in $Sm(OSiPh_3)_3(thf)_3$,[31] 2.13(2) Å in $Y(OSiPh_3)_3(thf)_3$,[32] 2.222(4) Å in $Ce(OSiPh_3)_3(thf)_3$,[33] and 2.225(7) Å in $La(OSiPh_3)_3(thf)_3$.[34] The differences in the above distances are close to those in their ionic radii.[35] There are only very few erbium siloxide complexes for comparison to be found in the literature. The triphenylsiloxide derivatives $Er(OSiPh_3)_3(thf)_3$ and $[Er(OSiPh_3)_2(\mu\text{-}OSiPh_3)]_2$ have been successfully employed for Er doping of lead zirconium titanate (PZT) ceramic thin films as well as for the production of Er_2O_3 nanoparticles. However, the compounds were not structurally authenticated by X-ray studies.[36] One notable example for a structurally verified complex comprising Er–O–Si bonds is the carborane species $[Na_2(thf)_{11}][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\mu\text{-}\eta^5{:}\sigma\text{-}(C_9H_6)SiMe_2O\}Er]_2$.[37] With 2.051(2) Å the Er–O(Si) distance in this compound is relatively short, indicating the presence of metal-d_π–oxygen-p_π interactions.[34]

Conclusions

We have shown that a seemingly straightforward reaction of an anhydrous lanthanide trichloride with the fully lithiated silsesquioxane precursor $(c\text{-}C_6H_{11})_7Si_7O_9(OLi)_3$ can take an unexpected course resulting in the formation of unusual heterodimetallic cluster complexes in fairly high yield. The facile coupling of two silsesquioxane cages in the coordination sphere of erbium opens the way to the construction of novel large bis(silsesquioxane) ligands.

Supporting Information (see footnote on the first page of this article): ORTEP drawings and X-ray structural data for **2**.

Acknowledgments

This work was generously supported by the Deutsche Forschungsgemeinschaft (SPP 1166 “Lanthanoid-spezifische Funktionalitäten in Molekül und Material”). Financial support by the Otto-von-Guericke-Universität Magdeburg is also gratefully acknowledged.

---

[1] Review articles: a) V. Lorenz, A. Fischer, S. Gießmann, J. W. Gilje, Yu. Gun′ko, K. Jacob, F. T. Edelmann, *Coord. Chem. Rev.* **2000**, *206–207*, 321; b) R. Duchateau, *Chem. Rev.* **2002**, *102*, 3525; c) R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.* **2004**, 675; d) V. Lorenz, F. T. Edelmann, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1147; e) V. Lorenz, F. T. Edelmann, *Adv. Organomet. Chem.* **2005**, *53*, 101.

[2] H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, *6*, 25.

[3] P. G. Harrison, *J. Organomet. Chem.* **1997**, *542*, 141.

[4] J. D. Lichtenhan, *Comments Inorg. Chem.* **1995**, *17*, 115.

[5] F. J. Feher, D. A. Newman, J. F. Walzer, *J. Am. Chem. Soc.* **1989**, *111*, 1741.

[6] M. G. Voronkov, V. L. Lavrentyev, *Top. Curr. Chem.* **1982**, *102*, 199.

[7] F. J. Feher, T. A. Budzichowski, R. L. Blanski, K. J. Keller, J. W. Ziller, *Organometallics* **1991**, *10*, 2526.

[8] F. J. Feher, T. A. Budzichowski, *Polyhedron* **1995**, *14*, 3239.

[9] P. G. Harrison, *J. Organomet. Chem.* **1997**, *542*, 141.

[10] R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev.* **1996**, *96*, 2205.

[11] T. W. Hambley, T. Maschmeyer, A. F. Masters, *Appl. Organomet. Chem.* **1992**, *6*, 253.

[12] J. Annand, H. C. Aspinall, A. Steiner, *Inorg. Chem.* **1999**, *38*, 1931.

[13] V. Lorenz, S. Giessmann, Y. K. Gun′ko, A. K. Fischer, J. W. Gilje, F. T. Edelmann, *Angew. Chem.* **2004**, *116*, 4703; *Angew. Chem. Int. Ed.* **2004**, *43*, 4603.

[14] F. J. Feher, T. A. Budzichowski, K. Rahimian, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3859.

[15] M. Crocker, R. H. M. Herold, A. G. Orpen, M. T. A. Overgaag, *J. Chem. Soc., Dalton Trans.* **1999**, 3791.

[16] K. Wada, M. Bundo, D. Nakabayashi, N. Itayama, T. Kondo, T. Mitsudo, *Chem. Lett.* **2000**, 628.

[17] M. Chabanas, E. A. Quadrelli, B. Fenet, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage, L. Emsley, *Angew. Chem.* **2001**, *113*, 4625; *Angew. Chem. Int. Ed.* **2001**, *40*, 4493.

[18] K. Wada, T. Mitsudo, *Yuki Gosei Kagaku Kyokaishi* **2006**, *64*, 836.

[19] H. C. L. Abbenhuis, A. D. Burrows, H. Kooijman, M. Lutz, M. T. Palmer, R. A. van Santen, A. L. Spek, *Chem. Commun.* **1998**, 2627.

[20] E. A. Quadrelli, J. E. Davies, B. F. G. Johnson, N. Feeder, *Chem. Commun.* **2000**, 1031.

[21] N. Maxim, A. Overweg, P. J. Kooijman, R. A. van Santen, H. C. L. Abbenhuis, *J. Mater. Chem.* **2002**, *12*, 3792.

[22] P. A. Shapley, W. S. Bigham, M. T. Hay, *Inorg. Chim. Acta* **2003**, *345*, 255.

[23] W. A. Herrmann, R. Anwander, V. Dufaud, W. Scherer, *Angew. Chem.* **1994**, *106*, 1338; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1285.

[24] J. Annand, H. C. Aspinall, A. Steiner, *Inorg. Chem.* **1999**, *38*, 3941.

[25] J. Annand, H. C. Aspinall, *J. Chem. Soc., Dalton Trans.* **2000**, 1867.

[26] P. L. Arnold, A. J. Blake, S. N. Hall, B. D. Ward, C. Wilson, *J. Chem. Soc., Dalton Trans.* **2001**, 488.

[27] Y. K. Gun′ko, R. Reilly, F. T. Edelmann, D. Stalke, *Angew. Chem.* **2001**, *113*, 1319; *Angew. Chem. Int. Ed.* **2001**, *40*, 1279.

[28] G. Wu, Y. Chen, D.-J. Xu, J.-C. Liu, W. Sun, Z. Shen, *J. Organomet. Chem.* **2009**, *694*, 1571.

[29] Preparation of **2**: The reaction was carried out under N_2 by using carefully dried solvents. $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (**1**, 4.1 mmol, 4.0 g)[5] was added to a solution of $LiN(SiMe_3)_2$, prepared in situ by reaction of butyllithium (7.9 mL of a 1.6 M solution in *n*-hexane) with $HN(SiMe_3)_2$ (2.6 mL, 2.03 g, 12.6 mmol) in thf (150 mL) at room temperature. The reaction mixture was stirred overnight. Then anhydrous $ErCl_3$ (1.12 g, 4.1 mmol) was added, followed by stirring for another 24 h. The solvents were evaporated in vacuo. The residue was extracted with *n*-pentane. Pale pink crystals of **2** (yield 3.2 g, 65%) were isolated after recrystallization from *n*-pentane. $C_{142}H_{262}Cl_2Er_2Li_4O_{38}Si_{22}$ (3628.7 g mol^{-1}): calcd. C 47.00, H 7.28; found C 45.95, H 6.77 (the low value for carbon might be traced back to silicon carbide formation). Decomposition > 105 °C. IR (KBr): $\tilde{\nu}$ = 2919 (vs), 2848 (vs), 1448 (s), 1346 [w, (δ_{CH2}, δ_{CH3})], 1269 (m), 1253 [m ($\nu_{Si\text{–}CH3}$)], 1197 [s ($\nu_{Si\text{–}C}$)], 1112 [vs (br.) + shoulders ($\nu_{Si\text{–}0}$, und $\nu_{C\text{–}0}$)], 933 (m), 894 (s), 847 (s), 824 (m), 754 (m), 685 (w), 640 [w (C–H wagging und rocking)], 515 (m), 463 (m), 418 (w) cm^{-1}. ^1H and ^{13}C NMR resonances could not be assigned due to strong broadening and shifting of the signals as an effect of the paramagnetic Er^{3+} ion. ^{29}SiNMR (79.5 MHz, $[D_8]$thf, 25 °C): δ = –27.5, –43.4, –66.3, –67.2, –68.0, –69.3, –69.5, –70.0 ppm.

[30] Data collection for **2**: $C_{137}H_{250}Cl_2Er_2Li_4O_{38}Si_{22}\cdot C_5H_{12}$, M_r = 3628.69, crystal dimensions 0.25 × 0.15 × 0.12 mm, triclinic ($P\bar{1}$), a = 15.0302(2) Å, b = 22.1228(3) Å, c = 30.2437(4) Å, α = 82.2600(10)°, β = 79.6990(10)°, γ = 83.4960(10)°, V = 9763.0(2) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.210 g/mm^3, μ = 1.077 mm^{-1}, Mo-K_α radiation, λ = 0.71073 Å, T = 103(2) K, reflections measured 202297, unique reflections 58784 (R_{int} = 0.0559), final R indices R_1 = 0.0639, wR_2 = 0.1234, largest difference peak and hole 1.846 and –2.097 e Å^{-3}. CCDC-770523 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[31] Z. Xie, K. Chui, Q. Yang, T. C. W. Mak, J. Sun, *Organometallics* **1998**, *17*, 3937.

[32] J. M. McGeary, P. S. Coan, K. Folting, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **1989**, *28*, 3283.

[33] P. B. Hitchcock, M. F. Lappert, A. Singh, *J. Chem. Soc., Chem. Commun.* **1983**, 1499.

[34] J. M. McGeary, P. S. Coan, K. Folting, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **1991**, *30*, 1723.

[35] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

[36] T. J. Boyle, L. A. M. Ottley, L. N. Brewer, J. Sigman, P. G. Clem, J. J. Richardson, *Eur. J. Inorg. Chem.* **2007**, 3805.

[37] S. Wang, Q. Yang, T. C. W. Mak, Z. Xie, *Organometallics* **1999**, *18*, 4478.

Received: February 16, 2010